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Jacques Hubert Olga Joseph WIJENBERG et al.

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For: BRAZING PRODUCT AND METHOD OF ITS MANUFACTURE

CLAIM FOR PRIORITY

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

The benefit of the filing date of the following prior foreign application filed in the following foreign country is hereby requested for the above-identified application and the priority provided in 35 USC 119 is hereby claimed:

European Patent Appln. No. 02078053.2, Filed 24 July 2002.

In support of this claim, a certified copy of said original foreign application is filed herewith.

It is requested that the file of this application be marked to indicate that the requirements of 35 USC 119 have been fulfilled and that the Patent and Trademark Office kindly acknowledge receipt of this document.

Respectfully submitted,

Date: Sept 28, 2007

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Patentanmeldung Nr. Patent application No. Demande de brevet n°

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Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
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Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se référer à la description.)

Brazing product and method of its manufacture

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BRAZING PRODUCT AND METHOD OF ITS MANUFACTURE

FIELD OF THE INVENTION

The invention relates to a brazing product, such as a brazing sheet product, comprising an aluminium layer being made of an aluminium alloy comprising silicon in an amount in the range of 4 to 14% by weight, and a further layer comprising nickel on the outer surface of said AlSi-alloy layer, wherein taken together said aluminium layer and all layers exterior thereto form a filler metal for a brazing operation. The invention also relates to a method of manufacturing such a brazing product, and to a brazed assembly comprising at least one component made of this brazing product.

DESCRIPTION OF THE RELATED ART

Aluminium and aluminium alloys can be joined by a wide variety of brazing and soldering processes. Brazing, by definition, employs a filler metal or alloy having a liquidus above 450°C and below the solidus of the base metal. Brazing is distinguished from soldering by the melting point of the filler metal: a solder melts below 450°C. Soldering processes are not within the field of the present invention.

Brazing products, and in particular brazing sheet products, find wide applications in heat exchangers and other similar equipment. Conventional brazing sheet products have a core or base sheet, typically an aluminium alloy of the Aluminium Association ("AA")3xxx-series, having on at least one surface of said core sheet clad an aluminium clad layer, the aluminium clad layer being made of an AA4xxx-series alloy comprising silicon in an amount in the range of 4 to 14% by weight, and preferably in the range of 7 to 14% by weight. The aluminium clad layer may be coupled to the core or base alloy in various ways known in the art, for example by means of roll bonding, cladding, explosive cladding, thermal spray-forming or semi-continuous or continuous casting processes.

Controlled Atmosphere Brazing ("CAB") and Vacuum Brazing ("VB") are the two main processes used for industrial scale aluminium brazing. Industrial vacuum brazing has been used since the 1950's, while CAB became popular in the early 1980's after the introduction of the NOCOLOK (trade mark) brazing flux. Vacuum brazing is an essentially discontinuous process and puts high demands on material cleanliness. The disruption of the aluminium oxide layer present is mainly caused by

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the evaporation of magnesium from the clad alloy. There is always more magnesium present in the furnace than necessary. The excess magnesium condenses on the cold spots in the furnace and has to be removed frequently. The capital investment for suitable equipment is relatively high.

5 CAB requires an additional process step prior to brazing as compared to VB, since a brazing flux has to be applied prior to brazing. A brazing flux for use in brazing aluminium alloys usually consist of mixtures of alkali earth chlorides and fluorides, sometimes containing aluminium fluoride or cryolite. CAB is essentially a continuous process in which, if the proper brazing flux is being used, high volumes
10 of brazed assemblies can be manufactured. The brazing flux dissolves the oxide layer at brazing temperature allowing the clad alloy to flow properly. When the NOCOLOK flux is used the surface needs to be cleaned thoroughly prior to flux application. To obtain good brazing results the brazing flux has to be applied on the total surface of the brazed assembly. This can cause difficulties with certain types of
15 assemblies because of their design. For example, because evaporator type heat exchangers have a large internal surface, problems can arise because of poor access to the interior. For good brazing results the flux has to adhere to the aluminium surface before brazing. Unfortunately the brazing flux after drying can easily fall off due to small mechanical vibrations. During the brazing cycle, corrosive fumes such
20 as HF are generated. This puts a high demand on the corrosion resistance of the materials applied for the furnace.

Ideally, a material should be available that can be used for CAB but does not have the requirements and defects of the known brazing flux application. Such a material can be supplied to a manufacturer of brazed assemblies and is ready to use
25 directly after forming of the assembly parts. No additional brazing fluxing operations have to be carried out. Presently, only one process for fluxless brazing is used on an industrial scale. The material for this process can be for example standard brazing sheet made from an AA3xxx-series core alloy clad on one or both sides with a cladding of an AA4xxx-series alloy. Before the brazing sheet can be used the surface
30 has to be modified in such a way that the naturally occurring aluminium oxide layer does not interfere during the brazing cycle. The method of achieving good brazing is to deposit a specific amount of nickel on the surface of the clad alloy. If properly

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applied, the nickel reacts, presumably exothermically, with the underlying aluminium. When electroplating is used the adherence of the nickel should be sufficient to withstand typical shaping operations being used in for example heat exchanger manufacture.

5 Processes for nickel-plating in an alkaline solution of aluminium brazing sheet are known from each of US-A-3,970,237, US-A-4,028,200, and US-A-4,164,454. According to these documents, nickel or cobalt, or combinations thereof, are most preferably deposited in combination with lead. The lead addition is used to improve the wettability of the aluminium clad alloy during the brazing cycle. An important
10 characteristic of these plating processes is that the nickel is preferentially deposited on the silicon particles of the aluminium clad alloy. To obtain sufficient nickel for brazing, the surface of the aluminium clad alloy should contain a relatively large number of silicon particles to act as nuclei for the nickel deposition. It is believed that to obtain sufficient nucleation sites a part of the aluminium in which the silicon
15 particles are embedded should be removed before pickling by chemical and/or mechanical pre-treatment. This is believed a necessary condition to obtain sufficient silicon coverage to serve as nuclei for the plating action of the brazing or clad alloy. On a microscopic scale the surface of the Si-containing cladding of the brazing sheet is covered with nickel-lead globules. However, the use of lead for the production of a
20 suitable nickel and/or cobalt layer on brazing sheet has several disadvantages. The use of lead for manufacturing products, such as automotive products, is undesirable and it is envisaged that in the very near future there might possibly even be a ban on lead comprising products or products manufactured via one or more intermediate processing steps comprising lead or lead-based components.

25 The international PCT patent application no. WO-00/71784, J.N. Mooij *et al.* discloses a brazing sheet product and a method of its manufacture. In this brazing sheet product there is provided a very thin bonding layer, preferably applied by plating, comprising zinc or tin between the AlSi-alloy clad layer and the nickel layer in order to improve the bonding of the nickel layer. The addition of lead to the nickel
30 layer has been replaced by the addition of bismuth while maintaining the excellent brazeability characteristics of the brazing sheet product.

A drawback of the known brazing sheet products having a layer comprising

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nickel is the limited corrosion life of brazed products in a SWAAT-test in accordance with ASTM G-85. Corrosion lifetimes without perforations are typically in the range of 4 days and thereby restricting possible interesting applications of the brazing product. For several applications of the known nickel-plated brazing sheet in
5 brazed products such a relatively short corrosion lifetime is not detrimental. However, a good corrosion resistance is considered a valuable property for brazing products used in amongst others heat exchangers, such as radiators and condensers. These heat exchangers are exposed to a severe external corrosive attack by e.g. de-icing road salt.

10 SUMMARY OF THE INVENTION

It is an object of the present invention to provide a Ni-plated brazing sheet product for use in a brazing operation, ideally a fluxless CAB brazing operation, and wherein the brazing sheet product has an improved post-braze corrosion resistance when measured in a SWAAT-test in accordance with ASTM G-85.

15 It is another object of the present invention to provide a brazing sheet product comprising a core sheet made of an aluminium alloy coupled on at least one surface of said core sheet to an aluminium clad layer, the aluminium clad layer being made of an aluminium alloy comprising silicon in an amount in the range of 4 to 14% by weight, and a further layer comprising nickel on the outer surface of said aluminium
20 clad layer such that taken together said aluminium clad layer and all layers exterior thereto form a filler metal for a brazing operation, and wherein the brazing sheet product has an improved post-braze corrosion resistance when measured in a SWAAT-test in accordance with ASTM G-85.

It is a further object of the present invention to provide a method of
25 manufacturing the brazing product, ideally in the form of a sheet product.

In accordance with the invention in one aspect there is provided a brazing sheet product comprising a core sheet, on at least one side of said core sheet a clad layer made of an aluminium alloy containing silicon in an amount in the range of 4 to 14% by weight, and on at least one outersurface of said clad layer a diffusion layer
30 comprising nickel-tin alloy.

By the addition of tin as important alloying element to the filler metal in the appropriate mol-ratio with respect to the nickel an improved corrosion performance

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is being obtained of the brazing product in a post-braze condition. In the brazing product according to the invention post-braze corrosion lifetimes without perforations according to ASTM G-85 exceed 7 days. The product can be fluxless brazed under controlled atmosphere conditions in the absence of a brazing flux
5 material while achieving very good post-braze corrosion performance enhancing the possibilities of application of the Ni-plated brazing product.

The invention is based in part on the insight that it is believed that the cathodic reaction governs the overall corrosion rate of Ni-plated brazing products when tested in the SWAAT-test in accordance with ASTM G-85. It is speculated that the
10 cathodic reaction in this system appears to be the Hydrogen Evolution Reaction ("HER"). When Ni-plated brazing products such as brazing sheets are being subjected to a brazing operation, typically a fluxless CAB operation, small Ni-aluminide particles are being formed which are believed to catalyse the HER. By the addition of tin in a sufficient amount to the metal filler and having a lower exchange
15 current density for the HER as compared to nickel-aluminides the catalyse effect is reduced and the post-braze corrosion performance of the brazed product is being improved remarkably.

It is believed that an upper layer of pure tin metal is sensitive to progressive oxidation in pre-braze conditions under humid conditions, e.g. during transport of a
20 plated coil to a customer. The surface oxides formed adversely influence the brazing process. By providing the tin required to improve the post-braze corrosion performance in the form of a nickel-tin diffusion layer, preferably obtained by a diffusion annealing treatment, no free tin is available anymore and thereby avoiding the occurrence of the detrimental progressive oxidation of the tin. It has been found
25 that a Ni-Sn alloy layer forms a thin stable surface oxide film in air.

Preferably, between the Ni-Sn alloy diffusion layer and the clad layer there is present a layer of nickel or nickel-alloy, preferably lead-free from an environmental point of view, to initiate the reaction, presumably exothermic, with the underlying AlSi-alloy during the brazing operation. This reaction does not occur, or at least to a
30 significant lesser extent, if alloying elements such as tin in a too high amount are present. Therefore, the nickel layer between the clad layer and the Ni-Sn alloy diffusion layer comprises of 96% by weight or more of nickel, and is preferably tin-

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free. The thickness of this nickel layer does not need to be very large, and is preferably 0.4 micron at most. Said thin layer of nickel or nickel-alloy may optionally contain bismuth as an alloying element in a range of up to 4% by weight to lower the surface tension of the molten filler metal during a brazing operation.

5 In an embodiment of the brazing sheet product the AlSi-alloy clad layer and all layers exterior thereto form the metal filler for a brazing operation and have a composition with the proviso that the mol-ratio of Ni:Sn is in the range of 10:(0.5 to 9), and preferably in the range of 10:(0.5 to 6). When the mol-ratio is too low no significant improvement in the post-braze corrosion life may be found. It has been
10 found that if the mol-ratio becomes more than 10:6, than the brazeability becomes less efficient, while at a mol-ratio of more than 10:9 the brazeability becomes very poor.

In an embodiment the brazing sheet product according to the invention is further characterised by an optional thin layer comprising zinc as an intermediate
15 bonding layer between said outer surface of the AlSi-alloy clad layer and said thin layer comprising nickel or nickel-alloy. With the zinc comprising intermediate bonding layer a very effective bond between the AlSi-alloy clad layer and the thin layer comprising nickel is formed, the bond remaining effective during subsequent deformation of the brazing product, for example in a bending operation. Preferably
20 the intermediate bonding layer has a thickness of at most 0.5µm, more preferably at most 0.3µm (300nm), and most preferably in the range of 0.01 to 0.15µm (10-150nm). In the best results obtained a thickness of about 30nm has been used. It has been found that the thin bonding layer of zinc has no detrimental effect on the post-braze corrosion performance of the product according to the invention.

25 In an embodiment of the brazing sheet product the core sheet is an aluminium alloy, and is preferably of an AA3xxx, or AA5xxx, or AA6xxx-series aluminium alloy.

In accordance with the invention in another aspect there is provided a method of manufacturing of an aluminium brazing product, which method comprises the
30 steps of (a) providing an aluminium base substrate of an aluminium alloy comprising silicon in an amount in the range of 4 to 14% by weight, (b) plating a metal layer comprising nickel or nickel alloy onto at least one outersurface of said aluminium

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base substrate, (c) plating a further metal layer comprising tin or tin-alloy onto the
outersurface of the layer comprising nickel or nickel alloy, and (d) subjecting the
plated brazing product to an annealing treatment by holding the plated brazing
product at a temperature in the range of 100 to 500°C for a period of 1 sec. to 300
5 minutes to form a diffusion layer comprising nickel-tin alloy.

The annealing treatment achieves the effect that the applied tin layer diffuses
into the applied nickel layer to form a Ni-Sn alloy layer. It is believed that an upper
layer of pure tin metal is sensitive to progressive oxidation in pre-braze conditions
under humid conditions. The surface oxides formed adversely influence the brazing
10 process. By providing the tin required to improve the post-braze corrosion
performance in the form of a nickel-tin diffusion layer essentially no free tin is
available anymore and thereby avoiding the occurrence of the detrimental
progressive oxidation of the tin. It has been found that a Ni-Sn alloy layer forms a
thin stable surface oxide film in air. Further oxidation in air takes essentially place
15 only at temperatures above about 320°C.

The melting point of tin is about 232°C. The annealing treatment may be
carried out below the melting temperature of tin, but requiring prolonged soaking
time up to 300 minutes. The annealing treatment may be carried out also above the
melting temperature of tin, for example at about 250°C or about 300°C, whereby the
20 tin diffuses into the solid nickel or nickel-alloy layer. Preferred annealing treatments
are at a temperature in a range of 230 to 350°C for a soaking time of 1 sec. to 600
sec., and more preferably 1 sec. to 300 sec.

The annealing treatment is preferably carried out in a protective environment
preventing the oxidation of tin or tin-alloy, such as a dry air atmosphere, or nitrogen
25 gas atmosphere or an HN_x -atmosphere or argon gas atmosphere or combinations
thereof.

In an embodiment taken together said aluminium base substrate and all layers
exterior thereto form a metal filler for a brazing operation and together has a
composition comprising at least, by weight percent:

- 30 Si in the range of 5 to 14 %,
Ni in the range of 0.03 to 8%,
Sn in the range of 0.01 to 7%,

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Bi in the range of at most 0.3%,

Sb in the range of at most 0.3%,

Zn in the range of at most 0.3%,

Mg in the range of at most 5%,

5 balance aluminium and inevitable impurities,

and with the proviso that the mol-ratio of Ni:Sn is in the range of 10:(0.5 to 9), and preferably in the range of 10:(0.5 to 6).

10 A typical impurity element in the filler metal is iron, in particular originating from the AlSi-alloy substrate or AlSi-alloy clad layer, and which may be tolerated up to about 0.8 %. Other alloying elements may be present, and will typically originate from the aluminium base substrate or alternatively the aluminium clad layer. Typically each impurity element is present in a range of not more than 0.05 %, and the total of the impurity elements does not exceed 0.3%.

15 When the mol-ratio is too low no significant effect on the post-braze corrosion life may be found. If the mol-ratio of Ni:Sn becomes more than 10:6, than the brazeability becomes less efficient, while at a mol-ratio of more than 10:9 the brazeability becomes very poor.

20 Depending on the Ni:Sn ratio applied, the diffusion annealing treatment is to form also a layer comprising nickel on the outersurface of said aluminium base substrate layer and the diffusion layer comprising nickel-tin alloy on the outersurface of said layer comprising nickel. During the diffusion annealing treatment the plated tin diffuses from above into the plated nickel or nickel-alloy layer, thereby leaving part of the underlying nickel layer located close to the clad layer unalloyed. This unalloyed nickel layer, or at least not alloyed with tin, is preferred since it is believed
25 that its is required to initiate the reaction, presumably exothermic, with the underlying AlSi-alloy during the brazing operation. This reaction does to a significant lesser extent occur, if alloying elements such as tin in a too high amount are present. The diffusion annealed Ni-Sn alloy layer has typically a thickness in the range of about 0.2 to 0.6µm.

30 Preferably in the brazing product according to the invention the plated layer comprising nickel or nickel-alloy having 90% or more of nickel, e.g. Ni-Bi, has a thickness of at most 2.0µm, preferably at most 1.0µm, and more preferably in the

range of 0.05 to 0.5 μ m. A coating thickness of more than 2.0 μ m requires a prolonged treatment time for plating, and may result in wrinkling of the molten filler metal during a subsequent brazing operation. A preferred minimum thickness for this nickel containing layer is about 0.25 μ m. Also other techniques such as dipping, thermal spraying, CVD, PVD or other techniques for depositing of metals or metal alloys from a gas or vapour phase may be used. Preferably the nickel comprising layer is essentially lead-free.

In the brazing product according to the invention the layer comprising tin or tin-alloy having 90% or more of tin, has a thickness prior to the diffusion annealing adjusted to the desired mol-ratio of Ni:Sn. This tin layer is preferably applied by means of plating. But also other techniques such as dipping, thermal spraying, CVD, PVD or other techniques for depositing of metals or metal alloys from a gas or vapour phase may be used.

In an embodiment the brazing product is elongated aluminium alloy stock, e.g. aluminium alloy sheet or strip, aluminium alloy wire or aluminium alloy rod.

In an embodiment the aluminium substrate is made of an AA4xxx-series aluminium alloy sheet or strip having Si as the most important alloying element in the range of 4 to 14% by weight, more preferably 7 to 14%, and can be plated on one or both surfaces with Ni or Ni-alloy, e.g. Ni-Bi alloy, and may be employed in subsequent brazing operations, in particular in an inert atmosphere brazing operation in the absence of a brazing-flux material. In the AA4xxx-series alloy other alloying elements may be present to improve specific properties, such as Mg up to 5%, the balance is made by impurities each up to 0.05 wt.%, total up to 0.25 wt.%, and aluminium. Iron may usually be present as impurity in an amount of up to 0.8 wt.%.

Also, aluminium alloy wire or rods being made of an AA4xxx-series alloy may be plated with a Ni or Ni-alloy layer having 90% or more of nickel, e.g. Ni-Bi alloy, and subsequently employed in a brazing operation, in particular in an inert atmosphere brazing (CAB) operation in the absence of a brazing-flux material, and may also be employed as weld filler wire or weld filler rod in a welding operation.

In an embodiment the aluminium substrate is an aluminium alloy sheet coupled to a core sheet made of an aluminium alloy. In a further embodiment the AlSi-alloy

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clad layer has a thickness ranging from about 2 to 20% of the total thickness of the total brazing product thickness. Typical aluminium clad layer thickness is in the range of 40 to 80 micron. The aluminium core sheet has a thickness typically in a range of at most 5 mm, more preferably in the range of 0.1 to 2 mm.

5 In an embodiment the method according to the invention is further characterised by depositing a thin layer comprising zinc as an intermediate bonding layer between said outersurface of said AlSi-alloy layer and said thin layer comprising nickel or nickel-alloy. With the intermediate bonding layer a very effective bond between the AlSi-alloy layer and the thin layer comprising nickel is
10 formed, the bond remaining effective during subsequent deformation of the brazing product, for example in a bending operation. The most suitable methods of applying such an intermediate layer of zinc is by means of direct or immersion plating. Preferably the applied intermediate bonding layer has a thickness of at most $0.5\mu\text{m}$, more preferably at most $0.3\mu\text{m}$ (300nm), and most preferably in the range of 0.01 to
15 $0.15\mu\text{m}$ (10-150nm). In the best results obtained a thickness of about 30nm has been used. A coating thickness of more than $0.5\mu\text{m}$ is thought to have no further advantages for improving the adhesion.

The invention further provides an assembly of components, for example a heat exchanger, typically for automotive applications, or a fuel cell, typically an
20 electrochemical fuel cell, joined by brazing, whereby at least one of said components being a brazing sheet product as set out above or the brazing product obtained by the method set out above. The brazing operation is preferably carried out in an inert atmosphere (CAB) in the absence of a brazing flux material or under a vacuum.

In an embodiment there is provided a brazed assembly wherein at least one of
25 the components to be joined by brazing is made of the brazing sheet product set out above or produced by the method in accordance with the invention described above, and at least one other component is made of steel, aluminized steel, stainless steel, plated or coated stainless steel, bronze, brass, nickel, nickel alloy, titanium, or plated or coated titanium.

30 BRIEF DESCRIPTION OF THE DRAWING

The invention will now be illustrated by a non-limitative example and with reference to the drawing, wherein:

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Fig 1. is a schematic longitudinal section showing the structure of a brazing sheet product according to the invention after a diffusion annealing treatment. Fig. 1 shows schematically a brazing product, in the present case aluminium brazing sheet, in accordance with the present invention consisting of a core sheet 1 on one or both sides clad with an aluminium clad layer 2 comprising an Al-Si alloy (also known as aluminium base substrate) and the nickel-tin alloy diffusion layer 3 resulting from the diffusion annealing treatment of two separately applied metal layers of nickel or nickel-alloy and tin or tin-alloy, and the layer 4 comprising nickel or nickel-alloy which has not been alloyed as a result of the diffusion annealing treatment, and the optional bonding layer 5 of zinc is applied, the advantages of which are set out above. In Fig. 1 the layers 3, 4 and 5 have been shown on only one side of the brazing sheet, but it will be immediately apparent to the skilled person that they may also be applied on both sides of the brazing sheet product. Thus, if desired, the clad layer 2 shown to only contact the core 1, may be further provided with other layers, e.g. 3 and 4, and optionally also with 5.

EXAMPLE

On a laboratory scale tests were carried out on aluminium brazing sheets manufactured from an AA3003 core alloy roll clad on both sides with an AA4045 clad alloy, and having a total thickness of 0.5 mm and a clad layer thickness of 50 microns on both sides. The following sequential pre-treatment steps have been used for each sample:

- cleaning by immersion for 180 sec. at 50°C in ChemTec 30014 (a commercial available bath), followed by rinsing,
- alkaline etching for 20 sec. at 50°C in ChemTec 30203 (a commercial available bath), followed by rinsing,
- desmutting for 60 sec. at room temperature in an acidic oxidising solution, typically 50% nitric acid, followed by rinsing,
- zincate immersion using ChemTec 19023 (a commercial available zincate bath) for 60 sec. at room temperature resulting in a thin zinc layer having a thickness of about 30 nm, followed by rinsing.

Following the above pre-treatment on both sides firstly a nickel layer of 0.5

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micron thickness (4.45 g/m^2) was applied by means of electroplating, and on top of the applied nickel layer a tin layer was applied also by means of electroplating of various thickness of 0.9, 1.8 and 3.0 g/m^2 (see Table 1).

The composition of nickel plating bath was a known Wath-bath comprising:

- 5 270 g/l $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$
- 50 g/l $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$
- 30 g/l H_3BO_3

The tin plating bath was a commercial available Methane Sulfonic Acid ("MSA") bath called RONAStan (trade mark) supplied by Shipley Ronal, and having the

10 composition:

- 25 g/l Sn
- 60 g/l MSA of 0.84 M.
- 3.5 g/l sulphuric acid
- 45 ml/l additive TP
- 15 4.5 ml/l anti-oxidant TP

Following the plating of the metal layers, the plated brazing sheet product was diffusion annealed for 8 minutes at 250°C under a protective inert nitrogen atmosphere to form a Ni-Sn diffusion layer. The diffusion annealed panels looked silvery and shiny. Samples of the diffusion-annealed products were analysed by

20 Glow Discharge Optical Emission Spectroscopy ("GDOES"). The GDOES depth profiles showed that the tin was completely alloyed with the nickel after the diffusion annealing treatment. There was no free tin present anymore. The resulting Ni-Sn alloy diffusion layer was mainly composed of the equilibrium phase Ni_3Sn_4 . Underneath the Ni-Sn alloy diffusion layer there was a tin-free nickel layer of about

25 0.35 micron thick and having the composition of the originally plated nickel layer prior to the diffusion annealing treatment and had not been alloyed with the tin as result of the diffusion annealing treatment. Repeating the diffusion annealing at 250°C in open air did not result in the detection of any detrimental oxides.

The plated specimens have been tested for adhesion using the Erichsen dome

30 test (5mm), and the T-bend test. A value assessment is then given to the adhesion of poor, fair, or good. All samples tested had a good adhesion performance.

For the assessment of the post-braze corrosion resistance, the samples have

been subjected to a simulated brazing cycle. The samples were heated under flowing nitrogen, with heating from room temperature to 580°C, dwell time at 580°C for 2 minutes, cooling from 580°C to room temperature. All samples had an excellent brazeability. Following the brazing cycle four samples of each type of plated brazing sheet have been tested in a SWAAT until the first perforations expressed in days of testing appear according to ASTM G-85, and the individual results are given in Table 1. The dimensions of the samples for the SWAAT-test were 100mx50mm.

As a reference it is mentioned that typically aluminium brazing sheets manufactured from an AA3003 core alloy clad on both sides with an AA4045 clad alloy, and having a total thickness of 0.5 mm and a clad layer thickness of 50 microns each and devoid of any further metal layers have a SWAAT-test performance of more than 16 days without perforations.

As a further reference material also brazing sheet product (same core and clad layer composition and thickness) with a thin zinc bonding layer and only a NiBi-alloy electroplated layer manufactured according to the example of the international PCT application no. WO-01/88226, J.N. Mooij *et al.*, and incorporated herein by reference, has been tested for its corrosion performance.

Table 1. Post-braze SWAAT-test results.

Sample no.	Alloy System	Amount of Sn (g/m ²)	at.-% Sn	Mol ratio Ni:Sn	Days till first perfor.	Average over 4 samples
1	NiBi	-	-	-	4	
2	NiBi	-	-	-	4	
3	NiBi	-	-	-	3	
4	NiBi	-	-	-	4	4
1	Ni+Sn	0.9	9.1	10:1	8	
2	Ni+Sn	0.9	9.1	10:1	5	
3	Ni+Sn	0.9	9.1	10:1	5	
4	Ni+Sn	0.9	9.1	10:1	6	6
1	Ni+Sn	1.8	16.7	10:2	7	
2	Ni+Sn	1.8	16.7	10:2	7	

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3	Ni+Sn	1.8	16.7	10:2	7	
4	Ni+Sn	1.8	16.7	10:2	8	7
1	Ni+Sn	3.0	25.0	10:3.33	8	
2	Ni+Sn	3.0	25.0	10:3.33	7	
3	Ni+Sn	3.0	25.0	10:3.33	8	
4	Ni+Sn	3.0	25.0	10:3.33	10	8

From the results of Table 1 it can be seen that a brazing sheet product known from the prior art and having a layer consisting of nickel with a small addition of bismuth as an alloying element has an average SWAAT-test result of 4 days. The application of a tin layer in an amount in accordance and after diffusion annealing in accordance with the invention results in a significant increase of the SWAAT-test performance, while maintaining a good adhesion performance and an excellent brazing performance. By increasing the amount of tin with respect to the amount of nickel an improved SWAAT-test performance is obtained. Tin may also reduce the surface tension of the molten metal filler during the brazing cycle and thereby improves the flowability of the molten filler metal. The amount of tin to improve on the post-braze corrosion performance is by far sufficient to overcome the need for the addition of bismuth or antimony or magnesium or lead added for the same purpose of reducing the surface tension. The combined addition of Sn with Bi and/or Sb and/or Mg and/or Pb remains still possible.

Having now fully described the invention, it will be apparent to one of ordinary skill in the art that many changes and modifications can be made without departing from the spirit or scope of the invention as hereon described.

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CLAIMS

1. A brazing sheet product comprising a core sheet (1), on at least one side of said core sheet (1) a clad layer (2) made of an aluminium alloy containing silicon in an amount in the range of 4 to 14% by weight, and on at least one outersurface of said clad layer (2) a diffusion layer (3) comprising nickel-tin alloy.
5
2. A brazing sheet product according to claim 1, wherein there is a layer (4) comprising nickel between the outersurface of said clad layer (2) and the diffusion layer (3).
10
3. A brazing sheet product according to claim 2, wherein there is a layer (5) comprising zinc as a bonding layer between said outersurface of said clad layer (2) and said layer comprising nickel (4).
15
4. A brazing sheet product according to claim 3, wherein said bonding layer (5) has a thickness of not more than 0.5 micron.
5. A brazing sheet product according to any one of claims 1 to 4, wherein the clad layer and all layers exterior thereto form a metal filler for a brazing operation and having a composition with the proviso that the mol-ratio of Ni:Sn is in the range of 10:(0.5 to 9).
20
6. A method of manufacturing of an aluminium brazing product, which method comprises the steps of (a) providing an aluminium base substrate layer of an aluminium alloy comprising silicon in an amount in the range of 4 to 14% by weight, (b) plating a metal layer comprising nickel or nickel-alloy onto at least one outersurface of said aluminium substrate, (c) plating a metal layer comprising tin or tin-alloy onto the outersurface of the layer comprising nickel or nickel-alloy, and (d) subjecting the plated brazing product to a diffusion annealing treatment by holding the plated brazing product at a temperature in the range of 100 to 500°C for a period of 1 sec. to 300 minutes to form on the
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outersurface of said aluminium base substrate a diffusion layer comprising nickel-tin alloy.

- 5 7. A method according to claim 6, wherein taken together the aluminium base substrate of an aluminium alloy comprising silicon in an amount in the range of 4 to 14% by weight and all layers exterior thereto form a metal filler for a brazing operation and having a composition comprising at least, by weight percent:
- 10 Si in the range of 5 to 14 %,
Ni in the range of 0.03 to 8%,
Bi in the range of at most 0.3%,
Sb in the range of at most 0.3%,
Sn in the range of 0.01 to 7%,
Zn in the range of at most 0.3%,
15 Mg in the range of at most 5%,
balance aluminium and inevitable impurities,
with the proviso that the mol-ratio of Ni:Sn is in the range of 10:(0.5 to 9).
- 20 8. A method according to claim 6 or 7, wherein the aluminium base substrate is made of an AA4000-series aluminium alloy.
- 25 9. A method according to any one of claims 6 to 8, wherein the aluminium base substrate is an aluminium alloy sheet coupled to a core sheet made of an aluminium alloy.
- 30 10. A method according to any one of claims 6 to 9, wherein prior to plating according to step (b), there is deposited onto the outersurface of the aluminium substrate a bonding layer comprising zinc said bonding layer having a thickness of not more than 0.5 micron, and preferably of not more than 0.3 micron.
11. A method according to any one of claims 6 to 9, wherein the diffusion

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annealing treatment is to form a layer comprising nickel on the outersurface of said aluminium base substrate layer and a diffusion layer comprising nickel-tin alloy on the outersurface of said layer comprising nickel.

- 5 12. An assembly of components joined by brazing, at least one said components being a brazing sheet product according to any one of claims 1 to 5, or the product obtained by the method according to any one of claims 6 to 11.

ABSTRACT

The invention relates to a brazing sheet product comprising a core sheet, a clad layer on said core sheet made of an aluminium alloy containing silicon in an amount in the range of 4 to 14% by weight, an optional layer comprising nickel on the outersurface of said clad layer, and a diffusion layer comprising nickel-tin alloy on the outer surface of said nickel layer. The invention further relates to a method of manufacturing such an brazing product comprising the process step of plating different metal layers and subjecting the plated brazing product to an annealing treatment by holding the plated brazing product at a temperature in the range of 100 to 500°C for a period of 1 sec. to 300 minutes to form a diffusion layer comprising nickel-tin alloy on the outer surface of said layer comprising nickel.

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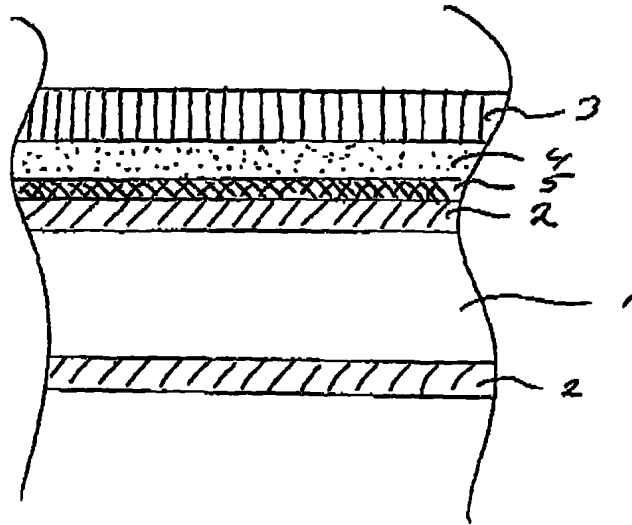


fig. 1